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<b>(21) International Application Number:</b> PCT/US98/22208 <b>(22) International Filing Date:</b> 22 October 1998 (22.10.98)  <b>(30) Priority Data:</b> 08/958,827                      28 October 1997 (28.10.97)                      US  <b>(71) Applicant:</b> PPG INDUSTRIES OHIO, INC. [US/US]; 3800 West 143rd Street, Cleveland, OH 44111 (US). <b>(72) Inventor:</b> PEKALA, Richard, W.; 3103 Henrich Farm Lane, Allison Park, PA 15101 (US). <b>(74) Agents:</b> MORRIS, George, D.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al.		<b>(81) Designated States:</b> CA, JP, MX, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> RADIATION CROSSLINKED PRINTING MEDIA  <b>(57) Abstract</b>  A process for producing a radiation crosslinked printing medium comprises: (a) coating a substrate with a coating composition comprising: (1) volatile aqueous solvent; (2) binder dissolved in the volatile aqueous solvent; (b) exposing the coated substrate to ionizing radiation to form a crosslinked coating; and (c) removing volatile aqueous solvent from the crosslinked coating. Preferably the binder comprises water-soluble poly(ethylene oxide) having no ethylenically unsaturated terminal groups, water-soluble poly(ethylene oxide) having at least some ethylenically unsaturated terminal groups, water-soluble poly(vinyl alcohol), water-soluble poly(vinylpyrrolidone), or a mixture of two or more thereof.		

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## RADIATION CROSSLINKED PRINTING MEDIA

Printing media suitable for inkjet printing are usually produced by coating a substrate with a coating composition comprising volatile aqueous solvent, water-soluble binder dissolved in the volatile aqueous solvent, and usually water-insoluble particles; and removing the aqueous solvent from the coating. A problem with this procedure is that the resulting coating remains water water-soluble.

10 A process has now been found which provides any desired degree of water-insolubility to the coating. Accordingly, one embodiment of the invention is a process comprising: (a) coating a substrate with a coating composition comprising: (1) volatile aqueous solvent;  
15 (2) water-soluble binder dissolved in the volatile aqueous solvent; (b) exposing the coated substrate to ionizing radiation to form a crosslinked coating; and (c) removing volatile aqueous solvent from the crosslinked coating.

Usually, but not necessarily, the binder comprises  
20 water-soluble poly(ethylene oxide) having no ethylenically unsaturated terminal groups, water-soluble poly(ethylene oxide) having at least some ethylenically unsaturated terminal groups, water-soluble poly(vinyl alcohol), water-soluble poly(vinylpyrrolidone), or a mixture of two or more thereof.

25 Another embodiment of the invention is a radiation crosslinked printing medium comprising: (a) a substrate having at least one surface; and (b) a crosslinked coating on the surface wherein the coating before crosslinking comprises water-soluble binder comprising water-soluble poly(ethylene  
30 oxide) having no ethylenically unsaturated terminal groups, water-soluble poly(ethylene oxide) having at least some ethylenically unsaturated terminal groups, water-soluble

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poly(vinyl alcohol), water-soluble poly(vinylpyrrolidone), or a mixture of two or more thereof.

The volatile aqueous solvent of the coating composition is predominately water. Small amounts of low boiling volatile water-miscible organic solvents may be intentionally added for particular purposes. Examples of such low boiling volatile water-miscible organic solvents include methanol [CAS 67-56-1], ethanol [CAS 64-17-5], 1-propanol, [CAS 71-23-8], 2-propanol [CAS 67-63-0], 2-butanol [CAS 78-92-2], 2-methyl-2-propanol [CAS 75-65-0], 2-propanone [CAS 67-64-1], and 2-butanone [CAS 78-93-3]. The listing of such solvents is by no means exhaustive.

It is preferred that substantially no low boiling volatile water-miscible organic materials be intentionally added to the system in order to minimize organic solvent emissions upon drying the coating.

Similarly, water-miscible organic solvents which are of low, moderate, or even negligible volatility may be intentionally added for particular purposes, such as for example, retardation of evaporation. Examples of such organic solvents include 2-methyl-1-propanol [CAS 78-83-1], 1-butanol [CAS 71-36-3], 1,2-ethanediol [CAS 107-21-1], and 1,2,3-propanetriol [CAS 56-81-5]. The listing of such solvents is by no means exhaustive.

It is preferred that substantially no water-miscible organic solvents which are of low, moderate, or negligible volatility be intentionally added to the system.

Notwithstanding the above, those materials which, although not intentionally added for any particular purpose, are normally present as impurities in one or more the components of the coating compositions of the invention and which become components of the solvent, may be present at low concentrations.

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In most instances water constitutes at least 80 percent by weight of the volatile aqueous solvent. Often water constitutes at least 95 percent by weight of the volatile aqueous solvent. Preferably water constitutes substantially all of the volatile aqueous solvent.

Water-soluble poly(ethylene oxide) having no ethylenically unsaturated terminal groups is known. It is ordinarily formed by polymerizing ethylene oxide [CAS 75-21-8], usually in the presence of a small amount of an initiator such as low molecular weight glycol or triol. Examples of such initiators include ethylene glycol [CAS 107-21-1], diethylene glycol [CAS 111-46-6], triethylene glycol [CAS 112-27-6], tetraethylene glycol [CAS 112-60-7], propylene glycol [CAS 57-55-6], trimethylene glycol [CAS 504-63-2], dipropylene glycol [CAS 110-98-5], glycerol [CAS 56-81-5], trimethylolpropane [CAS 77-99-6], and  $\alpha,\omega$ -diaminopoly(propylene glycol) [CAS 9046-10-0]. One or more other lower alkylene oxides such as propylene oxide [CAS 75-56-9] and trimethylene oxide [CAS 503-30-0] may also be employed as comonomer with the ethylene oxide, whether to form random polymers or block polymers, but they should be used only in those small amounts as will not render the resulting polymer both water-insoluble and nondispersible in water. As used herein and in the claims, the term "poly(ethylene oxide)" is intended to include the foregoing copolymers of ethylene oxide with small amounts of lower alkylene oxide, as well as homopolymers of ethylene oxide. The configuration of the poly(ethylene oxide) can be linear, branched, comb, or star-shaped. The preferred terminal groups of the poly(ethylene oxide) are hydroxyl groups, but terminal lower alkoxy groups such as methoxy groups may be present provided their types and numbers do not render the poly(ethylene oxide) polymer unsuitable for its purpose. The

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preferred poly(ethylene oxide) having no ethylenically unsaturated terminal groups is a water-soluble homopolymer of ethylene oxide produced using a small amount of ethylene glycol as an initiator.

5           The weight average molecular weight of the poly(ethylene oxide) having no ethylenically unsaturated terminal groups may vary widely. The weight average molecular weight of the poly(ethylene oxide) having no ethylenically unsaturated terminal groups is usually in the range of from  
10 100,000 to 3,000,000. Often the weight average molecular weight of the poly(ethylene oxide) having no ethylenically unsaturated terminal groups is in the range of from 150,000 to 1,000,000. Frequently the weight average molecular weight of the poly(ethylene oxide) having no ethylenically unsaturated  
15 terminal groups is in the range of from 200,000 to 1,000,000. From 300,000 to 700,000 is preferred.

Water-soluble poly(ethylene oxide) monomers having at least some ethylenically unsaturated terminal groups are also known materials. Examples include poly(ethylene oxide)  
20 monoacrylate [CAS 26403-58-7], poly(ethylene oxide) diacrylate [CAS 26570-48-9], poly(ethylene oxide) monomethacrylate [CAS 25736-86-1], and poly(ethylene oxide) dimethacrylate [CAS 25852-47-5]. Preparations of these materials are described in the following patent documents and elsewhere:  
25 US 3639459, SU 330159, JP 49-026227, JP 77-030489, JP 95-010801, DD 129778, DD 205891, DD 212035.

          The weight average molecular weight of the poly(ethylene oxide) monomers having at least some ethylenically unsaturated terminal groups may also vary  
30 considerably. The weight average molecular weight of the poly(ethylene oxide) monomers having at least some ethylenically unsaturated terminal groups is usually in the range of from 100,000 to 3,000,000. Often the weight average

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molecular weight of the poly(ethylene oxide) having no ethylenically unsaturated terminal groups is in the range of from 150,000 to 1,000,000. Frequently the weight average molecular weight of the poly(ethylene oxide) having no ethylenically unsaturated terminal groups is in the range of from 200,000 to 1,000,000. From 300,000 to 700,000 is preferred.

The water-soluble poly(vinyl alcohol) and its preparation are both well known. See Encyclopedia of Polymer Science and Technology, vol. 14, John Wiley & Sons, New York (1971), Library of Congress Catalog Card Number 64-22188, pages 149-207, the disclosure of which is incorporated herein by reference. Water-soluble poly(vinyl alcohol) is usually made either by (1) direct hydrolysis of a poly(vinyl ester) or (2) ester interchange with an alcohol such as methanol or ethanol. Other processes are known, but little used. All of these processes will hereinafter be referred to collectively as "hydrolysis". By far the most common poly(vinyl ester) used in these processes is poly(vinyl acetate). In most cases the poly(vinyl acetate) is a homopolymer, so that the poly(vinyl alcohol) is a homopolymer if hydrolysis is complete, or a copolymer of vinyl alcohol and vinyl acetate if hydrolysis is less than complete. Since vinyl acetate can be copolymerized with many other monomers, vinyl alcohol copolymers are readily available by the hydrolysis of the vinyl acetate copolymers. Irrespective of whether other monomers are copolymerized with the vinyl acetate (or other vinyl ester), the numbers of hydroxyl groups present in the resulting poly(vinyl alcohol) are sufficient to render the poly(vinyl alcohol) water-soluble. In most instances the water-soluble poly(vinyl alcohol) is characterized by a degree of hydrolysis of at least 75 percent. Often the water-soluble poly(vinyl alcohol) is characterized by a degree of hydrolysis

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of at least 80 percent. Preferably the degree of hydrolysis is at least 85 percent. As used herein and in the claims "degree of hydrolysis" is the ratio of the number of hydroxyl groups to the sum of the number of hydroxyl groups and the number of unreacted hydrolyzable ester groups present in the poly(vinyl alcohol), multiplied by one hundred. The degree of hydrolysis is expressed as percent.

The weight average molecular weight of the water-soluble poly(vinyl alcohol) may vary widely. In general, the weight average molecular weight should be at least as large as will permit the poly(vinyl alcohol) to form films, but not so large as will render the binder insoluble in the volatile aqueous solvent. Usually the weight average molecular weight of the water-soluble poly(vinyl alcohol) is in the range of from 100,000 to 400,000. Often the weight average molecular weight is in the range of from 110,000 to 300,000. From 120,000 to 200,000 is preferred.

Water-soluble poly(vinylpyrrolidone) is a known material and may be used. Usually, but not necessarily, the weight average molecular weight of the poly(vinylpyrrolidone) is in the range of from 1,000 to 3,000,000. Often the weight average molecular weight is in the range of from 5,000 to 1,000,000. From 5,000 to 500,000 is preferred.

The amount of water-soluble binder present in the binder of the coating composition before exposure to ionizing radiation may also vary widely. In most instances water-soluble poly(ethylene oxide) having no ethylenically unsaturated terminal groups, water-soluble poly(ethylene oxide) having at least some ethylenically unsaturated terminal groups, water-soluble poly(vinyl alcohol) or a mixture of two or more constitute from 70 to 100 percent by weight of the binder. Frequently these water soluble monomer(s) constitute from 85 to 100 percent by weight of the binder. From 95 to



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100 percent by weight is preferred. It is especially preferred that the water-soluble poly(ethylene oxide) having no ethylenically unsaturated terminal groups, water-soluble poly(ethylene oxide) having at least some ethylenically unsaturated terminal groups, water-soluble poly(vinyl alcohol) or a mixture of two or more constitute substantially all of the binder.

When water-soluble poly(ethylene oxide) having no ethylenically unsaturated terminal groups, water-soluble poly(ethylene oxide) having at least some ethylenically unsaturated terminal groups, water-soluble poly(vinyl alcohol), water-soluble poly(vinylpyrrolidone), or a mixture of two or more thereof are present in the water-soluble binder of the coating composition before exposure to ionizing radiation, their collectively amount may vary widely. In most instances water-soluble poly(ethylene oxide) having no ethylenically unsaturated terminal groups, water-soluble poly(ethylene oxide) having at least some ethylenically unsaturated terminal groups, water-soluble poly(vinyl alcohol), water-soluble (vinylpyrrolidone), or a mixture of two or more constitutes from 70 to 100 percent by weight of the binder. Frequently these water soluble monomer(s) constitute from 85 to 100 percent by weight of the binder. From 95 to 100 percent by weight is preferred. It is especially preferred that the water-soluble poly(ethylene oxide) having no ethylenically unsaturated terminal groups, water-soluble poly(ethylene oxide) having at least some ethylenically unsaturated terminal groups, water-soluble poly(vinyl alcohol), water-soluble poly(vinylpyrrolidone), or a mixture of two or more constitute substantially all of the water-soluble binder.

Water-soluble crosslinking agents may optionally be present in the binder of the coating composition. These

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crosslinking agents are water-soluble compounds which will react with one or more monomers of the binder upon exposure of a coating formed from the coating composition to ionizing radiation to cause crosslinking reactions to ensue. Examples  
5 of suitable water-soluble crosslinking agents include triacrylate-terminated ethoxylated trimethylolpropane, as for example Sartomer SR415 monomer (Sartomer Co., West Chester, Pennsylvania). Preferably when present the water-soluble crosslinking agent constitutes less than 5 percent by weight  
10 of the binder.

Minor amounts, usually less than 5 percent by weight, of other materials introduced for particular purposes may optionally be present in the binder. Examples of such optional materials include surfactants, antioxidants,  
15 ultraviolet light absorbers, dyes, and the like. The balance of the binder is substantially thermoplastic organic polymer.

All constituents of the binder of the coating composition are water-soluble. The water solubility of the binder of the coating of the printing medium is less than that  
20 of the coating composition due to crosslinks formed during exposure to ionizing radiation. As used herein and in the claims "water solubility" refers not only to the amount of polymer that can be dissolved in a given amount of water under equilibrium conditions, but also to the ease with which the  
25 polymer can be dissolved. The water solubility of the binder of the coating may vary widely and may be easily soluble, moderately soluble, difficultly soluble, or insoluble.

Usually, but not necessarily, the coating composition and the coating also comprise finely divided  
30 substantially water-insoluble filler particles. The finely divided substantially water-insoluble filler particles may be finely divided substantially water-insoluble inorganic filler particles, finely divided substantially water-insoluble

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thermoset organic polymer particles, finely divided substantially water-insoluble non-film-forming thermoplastic organic polymer particles, or a mixture of two or more thereof.

5           The finely divided substantially water-insoluble inorganic filler particles which may optionally be present are often finely divided substantially water-insoluble particles of thermoset organic polymer. Thermoset organic polymer is organic polymer crosslinked at least to the extent that it  
10 cannot be significantly softened or remelted by heat. Examples of such thermoset organic polymers include thermoset melamine-formaldehyde polymer, thermoset resorcinol-formaldehyde polymer, thermoset phenol-resorcinol-formaldehyde polymer, thermoset (meth)acrylate polymer, and thermoset  
15 styrene-divinylbenzene polymer.

          The discrete thermoplastic organic filler particles which may be present are thermoplastic in that they may be softened and/or melted at elevated temperatures. Nevertheless they are not film-forming when used in accordance with this  
20 invention. Examples of suitable discrete thermoplastic organic polymer particles include polyethylene particles such as those contained in Poly Emulsion 316N30 sol (ChemCor Inc., Chester, NY), maleated polypropylene particles such as those contained in Poly Emulsion 43C30 sol (ChemCor Inc.,  
25 Chester, NY), and polyacrylate, polymethacrylate, polystyrene, and/or fluoropolymer particles made by microemulsion processes.

          In most instances the finely divided substantially water-insoluble filler particles are finely divided  
30 substantially water-insoluble inorganic filler particles. The types of finely divided substantially water-insoluble inorganic filler particles are numerous and widely varied. The finely divided substantially water-insoluble inorganic

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filler particles which may optionally be present are often finely divided substantially water-insoluble particles of metal oxide. The metal oxide constituting the particles may be a simple metal oxide (i.e., the oxide of a single metal) or  
5 it may be a complex metal oxide (i.e., the oxide of two or more metals). The particles of metal oxide may be particles of a single metal oxide or they may be a mixture of different particles of different metal oxides.

Examples of suitable metal oxides include alumina,  
10 silica, and titania. Other oxides may optionally be present in minor amount. Examples of such optional oxides include, but are not limited to, zirconia, hafnia, and yttria. Other metal oxides that may optionally be present are those which are ordinarily present as impurities such as for example, iron  
15 oxide. For purposes of the present specification and claims, silicon is considered to be a metal.

When the particles are particles of alumina, most often the alumina is alumina monohydroxide. Particles of alumina monohydroxide,  $\text{AlO}(\text{OH})$ , and their preparation are  
20 known. The preparation and properties of alumina monohydroxide are described by B. E. Yoldas in The American Ceramic Society Bulletin, Vol. 54, No. 3, (March 1975), pages 289-290, in Journal of Applied Chemical Biotechnology, Vol. 23 (1973), pages 803-809, and in Journal of Materials  
25 Science, Vol. 10 (1975), pages 1856-1860. Briefly, aluminum isopropoxide or aluminum secondary-butoxide are hydrolyzed in an excess of water with vigorous agitation at from 75 C to 80°C to form a slurry of aluminum monohydroxide. The aluminum monohydroxide is then peptized at temperatures of at least  
30 80°C with an acid to form a clear alumina monohydroxide sol which exhibits the Tyndall effect when illuminated with a narrow beam of light. Since the alumina monohydroxide of the sol is neither white nor colored, it is not a pigment and does

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not function as a pigment in the present invention. The acid employed is noncomplexing with aluminum, and it has sufficient strength to produce the required charge effect at low concentration. Nitric acid, hydrochloric acid, perchloric acid, acetic acid, chloroacetic acid, and formic acid meet these requirements. The acid concentration is usually in the range of from 0.03 to 0.1 mole of acid per mole of aluminum alkoxide. Although it is desired not to be bound by any theory, it is believed that the alumina monohydroxide produced in this manner is pseudo-boehmite. Pseudo-boehmite is indeed the preferred alumina monohydroxide for use in the present invention. The alumina monohydroxide is not a pigment and does not function as a pigment in the present invention. In most instances the alumina monohydroxide is transparent and colorless.

Colloidal silica is also known. Its preparation and properties are described by R. K. Iler in The Chemistry of Silica, John Wiley & Sons, Inc., New York (1979) ISBN 0-471-02404-X, pages 312-337, and in United States Patents No. 2,601,235; 2,614,993; 2,614,994; 2,617,995; 2,631,134; 2,885,366; and 2,951,044, the disclosures of which are, in their entireties, incorporated herein by reference. Examples of commercially available colloidal silica include Ludox® HS, LS, SM, TM and CL-X colloidal silica (E. I. du Pont de Nemours & Company, Inc.) in which the counter ion is the sodium ion, and Ludox® AS colloidal silica (E. I. du Pont de Nemours & Company, Inc.) in which the counter ion is the ammonium ion. Another example is Ludox® AM colloidal silica (E. I. du Pont de Nemours & Company, Inc.) in which some of the silicon atoms have been replaced by aluminum atoms and the counter ion is the sodium ion.

Colloidal titania is also known. Its preparation and properties are described in United States Patent No.

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4,275,118. Colloidal titania may also be prepared by reacting titanium isopropoxide [CAS 546-68-9] with water and tetramethyl ammonium hydroxide.

The filler particles have a maximum dimension of less than 500 nanometers. Often the filler particles have a maximum dimension of less than 100 nanometers. Frequently the maximum dimension is less than 50 nanometers. Preferably the maximum dimension is less than 20 nanometers.

As used herein and in the claims the maximum dimension of the filler particles is determined by transmission electron microscopy.

When present, the amount of the finely divided substantially water-insoluble filler particles in the coating may vary widely. Often the finely divided substantially water-insoluble filler particles constitute from 20 to 80 percent by weight of the coating. In many cases the finely divided substantially water-insoluble filler particles constitute from 25 to 60 percent by weight of the coating. From 30 to 50 percent by weight is preferred.

The coating may be substantially transparent, substantially opaque, or of intermediate transparency. It may be substantially colorless, it may be highly colored, or it may be of an intermediate degree of color. Preferably the coating is substantially transparent and substantially colorless. As used herein and in the claims, a coating is substantially transparent if its luminous transmission in the visible region is at least 80 percent of the incident light. Often the luminous transmission of the coating is at least 85 percent of the incident light. Preferably the luminous transmission of the coating is at least 90 percent. Also as used herein and in the claims, a coating is substantially colorless if the luminous transmission is substantially the

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same for all wavelengths in the visible region, viz., 400 to 800 nanometers.

The thickness of the coating may vary widely, but in most instances the thickness of the coating is in the range of from 1 to 40  $\mu\text{m}$ . In many cases the thickness of the coating is in the range of from 5 to 40  $\mu\text{m}$ . Often the thickness is in the range of from 8 to 30  $\mu\text{m}$ . From 12 to 18  $\mu\text{m}$  is preferred.

The substrate may be any substrate at least one surface of which is capable of bearing the coating discussed above. In most instances the substrate is in the form of an individual sheet or in the form of a roll, web, strip, film, or foil of material capable of being cut into sheets.

The substrate may be porous throughout, it may be nonporous throughout, or it may comprise both porous regions and nonporous regions.

Examples of porous substrates include paper, paperboard, wood, cloth, nonwoven fabric, felt, unglazed ceramic material, microporous polymer membranes, microporous membranes comprising both polymer and filler particles, porous foam, and microporous foam.

Examples of substrates which are substantially nonporous throughout include sheets or films of organic polymer such as poly(ethylene terephthalate), polyethylene, polypropylene, cellulose acetate, poly(vinyl chloride), and copolymers such as saran. The sheets or films may be metallized or unmetallized as desired. Additional examples include metal substrates including but not limited to metal foils such as aluminum foil and copper foil. Yet another example is a porous or microporous foam comprising thermoplastic organic polymer which foam has been compressed to such an extent that the resulting deformed material is substantially nonporous. Still another example is glass.

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Base stocks which are normally porous such as for example paper, paperboard, wood, cloth, nonwoven fabric, felt, unglazed ceramic material, microporous polymer membranes, microporous membranes comprising both polymer and filler particles, porous foam, or microporous foam may be coated or laminated to render one or more surfaces substantially nonporous and thereby provide substrates having at least one substantially nonporous surface.

The substrate may be substantially transparent, it may be substantially opaque, or it may be of intermediate transparency. For some applications such as inkjet printed overhead slides, the substrate must be sufficiently transparent to be useful for that application. For other applications such as inkjet printed paper, transparency of the substrate is not so important.

The amount of volatile aqueous solvent present in the coating composition may vary very widely. In general, at least enough volatile aqueous solvent should be present to dissolve the binder. The maximum amount is not limited by any theory, but by practical considerations such as the time and cost to remove the volatile aqueous solvent from the coating after exposure to ionizing radiation. In most cases the volatile aqueous solvent constitutes from 80 to 99 percent by weight of the coating composition. Often the volatile aqueous solvent constitutes from 82 to 95 percent by weight of the coating composition. From 85 to 93 percent by weight is preferred.

The coating compositions of the invention are usually prepared by simply admixing the various ingredients. Although the mixing is usually accomplished at room temperature, elevated temperatures are sometimes used. The maximum temperature which is usable depends upon the heat



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stability of the ingredients. Temperatures above about 100°C are only rarely employed.

The coating compositions of the invention are generally used to form adherent coatings on substrates. The  
5 substrate is coated with the coating composition using substantially any technique known to the art. These include spraying, curtain coating, dipping, roller application, printing, brushing, drawing, and extrusion.

Substrates which may be coated with the coating  
10 compositions of the invention may vary widely in their identities and their properties. The substrate may be transparent or it may be opaque. Organic substrates such as wood, fiberboard, particle board, composition board, paper, cardboard and various polymers such as polyolefins (especially  
15 polyethylene and polypropylene), polyesters (especially poly(ethylene terephthalate)), polyamides, cured phenolic resins, cured aminoplasts, polystyrene, and poly(meth)acrylates. Inorganic substrates are exemplified by glass, quartz, and ceramic materials. Many metallic  
20 substrates may be coated. Exemplary metallic substrates are iron, steel, stainless steel, copper, brass, bronze, aluminum, magnesium, titanium, nickel, chromium, zinc, and alloys.

Once the coating has been applied to the substrate, it is exposed to ionizing radiation to reduce the water  
25 solubility of the binder.

The ionizing radiation employed in the invention is radiation possessing an energy at least sufficient to produce ions either directly or indirectly in a medium composed of common elements such as air or water and includes ionizing  
30 particle radiation and ionizing electromagnetic radiation. Ionizing particle radiation designates the emission of electrons or accelerated nuclear particles such as protons, alpha particles, deuterons, beta particles, neutrons, or their

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analogs. Charged particles can be accelerated using such devices as resonance chamber accelerators, DC potential gradient accelerators, betatrons, synchrotrons, cyclotrons, etc. Neutron radiation can be produced by bombarding a  
5 selected light metal such as beryllium with positively charged particles of high energy. Ionizing particle radiation can also be obtained by the use of an atomic pile, radioactive isotopes, or other natural or synthetic radioactive materials.

Ionizing electromagnetic radiation comprises high energy  
10 photons. Examples are X-rays, bremsstrahlung, and gamma rays.

X-rays may be produced when a metallic target such as tungsten, copper, or molybdenum is bombarded with electrons of suitable energy. This energy is conferred to the electrons by accelerators, usually, but not necessarily, of the linear  
15 type. Traveling wave linear accelerators, standing wave linear accelerators, and DC potential gradient linear accelerators are ordinarily employed for this purpose.

Bremsstrahlung, also known as continuous X-rays, is produced by the deceleration of electrons. The continuum  
20 extends from a short-wave limit dependent upon the maximum energy of the electrons indefinitely toward the long wavelength end of the spectrum.

Gamma rays may be obtained by means of a nuclear reactor, such as a pile, by the use of natural or synthetic  
25 radioactive materials such as cobalt 60 or radium which emit gamma rays, or by absorption of a neutron in the (n, $\gamma$ ) reaction.

The ionizing radiation, whether particle radiation or electromagnetic radiation, ordinarily has an energy of at  
30 least about 10 electron volts. While there is no upper limit to the energy of ionizing radiation which can be used advantageously, the effects desired in the practice of this invention can be accomplished without resorting to the use of

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ionizing radiation having energies above about 20,000,000 electron volts.

Accelerated electrons is the preferred ionizing radiation for crosslinking coatings of the radiation curable coating composition of the invention. Bremsstrahlung generated by the deceleration of the electrons is also present and probably contributes to crosslinking. Various types of linear electron accelerators are known, for example, the ARCO type traveling wave accelerator model Mark 1, operating at 3 to 10 million electron volts supplied by High Voltage Engineering Corporation, Burlington, Mass., or other types of accelerators such as are described in U.S. Patent No. 2,763,609 and British Patent Specification No. 762,953 are satisfactory for the practice of this invention. Usually the electrons are accelerated to energies in the range of from about 10,000 electron volts to about 1,000,000 electron volts.

Typically, the energy is in the range of from about 20,000 electron volts to about 500,000 electron volts. Preferably, the energy is in the range of from about 25,000 electron volts to about 200,000 electron volts.

The unit of dose of ionizing radiation is the "rad" which is equal to 100 ergs of energy absorbed from ionizing radiation per gram of material being irradiated. Dose is initially determined using an absolute method such as calorimetry or ionization dosimetry. These absolute methods are quite sophisticated and hence are not generally practical for routine determinations. Once a radiation field has been explored by an absolute method of dosimetry, it is possible to calibrate secondary radiation indicators in that field using relative dosimetry techniques.

In some instances, depending upon the monomer(s) involved, oxygen inhibits the free radical crosslinking of the exterior portion of the coating thereby leaving the coating

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surface under cured. In such instances exposure of the coating to ionizing radiation should be conducted in an atmosphere wherein any oxygen present is insufficient to significantly inhibit the free radical crosslinking of the exterior portion of the coating. Suitable atmospheres may be established using any unreactive gases for the purpose, as for example nitrogen, argon, or helium. When oxygen inhibition is not a problem, an atmosphere of air is generally employed although atmospheres having greater or lesser concentration of oxygen than air are satisfactory.

Coatings of the coating compositions of the invention are ordinarily exposed to ionizing radiation in an amount in the range of from about 0.01 megarad to about 20 megarads, although doses greater than 20 megarads may be used satisfactorily. The dose, however, should not be so great that the chemical or physical properties of the coating are seriously impaired. Typically, the dose is in the range of from about 0.1 megarad to about 20 megarads. The preferred dose is in the range of from about 1 megarad to about 10 megarads.

Once the water solubility of the binder has been reduced to the desired degree by exposure to ionizing radiation, aqueous solvent is removed from the coating. In most instances at least 80 percent of the aqueous solvent initially present in the coating as applied is removed after the coating has been exposed to ionizing radiation. Often at least 90 percent of the aqueous solvent initially present in the coating as applied is removed after the coating has been exposed to ionizing radiation. Preferably at least 95 percent is removed after exposure of the coating to ionizing radiation.

Removal of aqueous solvent from the coating is usually accomplished by drying at either ambient or elevated

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temperature. Ordinarily the drying temperatures are in the range of from 50°C to 125°C. Temperatures in the range of from 75°C to 105°C are preferred.

Other than in the operating examples, or where  
5 otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about".

The invention is further described in conjunction with the following examples which are to be considered  
10 illustrative rather than limiting, and in which all parts are parts by weight and all percentages are percentages by weight unless otherwise specified.

#### EXAMPLE 1

15 The charges shown in Table 1 were used in the preparation of a cationic acrylic polymer aqueous dispersion.

#### TABLE 1

<u>Ingredients</u>	<u>Weight, kilograms</u>
<u>Charge 1</u>	
Methyl ethyl ketone	55.93
<u>Charge 2</u>	
Methyl ethyl ketone	28.67
Initiator <sup>1</sup>	10.16
<u>Charge 3</u>	
n-Butyl acrylate	30.44
Methyl methacrylate	87.32
2-(tert-Butylamino)ethyl methacrylate	
[CAS 3775-90-4]	40.64
Styrene	44.68
<u>Charge 4</u>	
Methyl ethyl ketone	2.27

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TABLE 1 (continued)

	<u>Ingredients</u>	<u>Weight, kilograms</u>
5	<u>Charge 5</u> Methyl ethyl ketone	2.27
	<u>Charge 6</u> Glacial acetic acid	9.89
10	Methyl ethyl ketone	2.27
	<u>Charge 7</u> Deionized water	579.1
15	<u>Charge 8</u> Deionized water	11.1

20     <sup>1</sup> VAZO<sup>®</sup> 67 2,2'-Azobis(2-methylbutanenitrile) initiator,  
E. I. du Pont de Nemours and Company, Wilmington, Delaware.

Charge 1 was heated in a reactor with agitation to reflux temperature (80°C). The addition of Charge 2 from a catalyst tank to the reactor was then begun. The addition of Charge 2 was made over a period of 305 minutes. Five minutes after beginning the addition of Charge 2, the addition of Charge 3 from a monomer tank was begun. The addition of Charge 3 was made over a period of 240 minutes. When the addition of Charge 3 was completed, Charge 4 was added to the monomer tank as a rinse and then the rinse liquid was added from the monomer tank to the reactor over a period of 10 minutes. Upon completion of the addition of Charge 2, Charge 5 was added to the catalyst tank as a rinse and then the rinse liquid was added from the catalyst tank to the reactor over a period of 10 minutes. The reaction mixture was then agitated at reflux for three hours while the temperature of the reaction mixture was in the range of from 83°C to 86°C. At the end of the three hour period, the reaction mixture was cooled to temperatures in the range of from 48°C to 52°C. Charge 6 was added over a

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period of 10 minutes and the reaction mixture was thereafter agitated for 15 minutes. Charge 7 was added to a thinning tank equipped for distillation and heated to temperatures in the range of from 48°C to 52°C. The reaction mixture was dropped  
5 from the reactor to the thinning tank as quickly as possible. Charge 8 was added to the reactor as a rinse and then the rinse liquid was also dropped to the thinning tank. The contents of the thinning tank were agitated for 30 minutes at temperatures in the range of from 48°C to 52°C. Over a thirty minute period  
10 the pressure was reduced to 71.3 kilopascals, absolute. The temperature was then increased and liquid was stripped off under vacuum until the solids content of the batch was about 30 percent by weight. The resulting product which was a cationic acrylic polymer aqueous dispersion, was cooled to about  
15 48°C, filtered, and then discharged into drums.

A poly(ethylene oxide) (PEO) solution was formed by dissolving 180 grams poly(ethylene oxide) having a weight average molecular weight of about 400,000 in 2820 grams of deionized water. The mixture was stirred until all  
20 poly(ethylene oxide) was dissolved giving a composition containing 6.0 percent solids.

With stirring, 248 grams of aluminum tri-sec-butoxide [CAS 2269-22-9] was added to 2 liters of water at 70°C in a glass container. To this mixture 6 grams of  
25 60 percent concentrated nitric acid was added. The reaction mixture was stirred for 15 minutes on a hot plate. The glass container containing the reaction mixture was then sealed with a lid and placed in an oven at 95°C for 2 days. During the two day period in the oven the precipitate in the reaction  
30 mixture was peptized. The resulting colloidal dispersion was concentrated in an unsealed container to 600 grams by boiling to produce a colloidal dispersion (sol) containing 10 percent by weight colloidal alumina monohydroxide,  $\text{AlO}(\text{OH})$ .

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To 66.6 grams of the above PEO solution were added 32.7 grams of the above  $\text{AlO}(\text{OH})$  sol. The mixture was stirred to form a homogeneous coating composition.

The coating composition was applied to poly(ethylene terephthalate) (PET) film with a Meyer Rod #150. Immediately after application of the coating, the coated side of the PET film was passed under an electron beam to provide an exposure of 5 Megarads. The resultant film was then placed in a circulating oven at  $85^{\circ}\text{C}$  to remove water from the crosslinked coating. The dry coating was approximately 20 micrometers thick.

The above film was then printed on the coated side by a Hewlett-Packard 1600C ink jet printer. The printed film showed good image quality.

#### EXAMPLE 2

To a mixture containing 50.0 grams of a poly(ethylene oxide) solution and 32.7 grams of  $\text{AlO}(\text{OH})$  sol, each prepared as described in Example 1, were added 1.0 grams of glycerol-tris-[poly(propylene glycol), amine terminated] ether [Aldrich Chemical Co.; CAS 64852-22-8] and an additional 15.0 grams of deionized water. The mixture was stirred to form a homogeneous coating composition.

The coating composition was applied to poly(ethylene terephthalate) (PET) film with a Meyer Rod #150. Immediately after application of the coating, the coated side of the PET film was passed under an electron beam to provide an exposure of 5 Megarads. The resultant film was then placed in a circulating oven at  $85^{\circ}\text{C}$  to remove water from the crosslinked coating. The dry coating was approximately 20 micrometers thick.



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The above film was then printed on the coated side by a Hewlett-Packard 1600C ink jet printer. The printed film showed good image quality.

5

EXAMPLE 3

To 50.0 grams of a poly(ethylene oxide) solution prepared as described in Example 1 were added 10.0 grams of a 30 percent cationic maleated polypropylene (PP) sol (POLY EMULSION 43C30; ChemCor Inc., Chester, NY). Next, 10.3 grams of the above cationic acrylic polymer aqueous dispersion were added to the above mixture. Finally, 1.0 grams of poly(ethylene glycol-400) dimethacrylate [Aldrich Chemical Co.; CAS 25852-47-5] and 15.0 grams of deionized water were added to the above mixture with stirring to form a homogeneous coating composition.

The coating composition was applied to poly(ethylene terephthalate) (PET) film with a Meyer Rod #150. Immediately after application of the coating, the coated side of the PET film was passed under an electron beam to provide an exposure of 5 Megarads. The resultant film was then placed in a circulating oven at 85°C to remove water from the crosslinked coating. The dry coating was approximately 20 micrometers thick.

The above film was then printed on the coated side by a Hewlett-Packard 1600C ink jet printer. The printed film showed good image quality.

EXAMPLE 4

A poly(vinyl pyrrolidone) (PVP) solution was formed by dissolving 20 grams of Luviskol® K-90 [BASF Corp.] in 180 grams of deionized water. The mixture was stirred until all poly(vinyl pyrrolidone) was dissolved giving a composition containing 10.0 percent solids.

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To 55.0 g of the above PVP solution were added 55.0 grams of the  $\text{AlO}(\text{OH})$  sol described in Example 1. The mixture was stirred to form a homogeneous coating composition.

The coating composition was applied to poly(ethylene terephthalate) (PET) film with a Meyer Rod #150. Immediately after application of the coating, the coated side of the PET film was passed under an electron beam to provide an exposure of 2.5 Megarads. The resultant film was then placed in a circulating oven at 85°C to remove water from the crosslinked coating. The dry coating was approximately 20 micrometers thick.

The above film was then printed on the coated side by a Hewlett-Packard 850C ink jet printer. The printed film showed good image quality.

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#### EXAMPLE 5

To 50.0 grams of a poly(ethylene oxide) solution prepared as described in Example 1 were added 12.8 grams of a 24.5 percent by weight  $\text{AlO}(\text{OH})$  sol (Nyacol AL-20; PQ Corp.) and 10.9 grams of the above cationic acrylic polymer aqueous dispersion. The mixture was stirred to form a homogeneous coating composition.

The coating composition was applied to poly(ethylene terephthalate) (PET) film with a Meyer Rod #150. Immediately after application of the coating, the coated side of the PET film was passed under an electron beam to provide an exposure of 2.5 Megarads. The resultant film was then placed in a circulating oven at 85°C to remove water from the crosslinked coating. The dry coating was approximately 20 micrometers thick.

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The above film was then printed on the coated side by a Hewlett-Packard 850C ink jet printer. The printed film showed good image quality.

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Although the present invention has been described with reference to specific details of certain embodiments thereof, it is not intended that such details should be regarded as limitations upon the scope of the invention except  
5 insofar as they are included in the accompanying claims.

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## CLAIMS:

1. A process comprising:
  - (a) coating a substrate with a coating composition comprising:
    - (1) volatile aqueous solvent;
    - (2) binder dissolved in the volatile aqueous solvent;
  - (b) exposing the coated substrate to ionizing radiation to form a crosslinked coating; and
  - (c) removing volatile aqueous solvent from the crosslinked coating.
2. The process of claim 1 wherein the binder comprises water-soluble poly(ethylene oxide) having no ethylenically unsaturated terminal groups, water-soluble poly(ethylene oxide) having at least some ethylenically unsaturated terminal groups, water-soluble poly(vinyl alcohol), water-soluble poly(vinylpyrrolidone), or a mixture of two or more thereof.
3. The process of claim 1 wherein the volatile aqueous solvent constitutes from 80 to 99 percent by weight of the coating composition.
4. The process of claim 1 wherein the coating composition comprises finely divided substantially water-insoluble filler particles having a maximum dimension of less than 500 nanometers.
5. The process of claim 4 wherein the finely divided substantially water-insoluble filler particles are finely divided substantially water-insoluble inorganic filler

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particles, finely divided substantially water-insoluble thermoset organic polymer particles, finely divided substantially water-insoluble non-film-forming thermoplastic organic polymer particles, or a mixture of two or more thereof.

6. The process of claim 4 wherein the finely divided substantially water-insoluble filler particles are particles of pseudoboehmite.

7. The process of claim 1 wherein the coated substrate is exposed to a dose of ionizing radiation in the range of from 0.01 to 20 megarads.

8. The process of claim 1 wherein the ionizing radiation is accelerated electrons.

9. The process of claim 1 wherein the substrate is an organic substrate.

10. A radiation crosslinked printing medium comprising:

- (a) a substrate having at least one surface; and
- (b) a crosslinked coating on the surface wherein the coating before crosslinking comprises water-soluble binder comprising water-soluble poly(ethylene oxide) having no ethylenically unsaturated terminal groups, water-soluble poly(ethylene oxide) having at least some ethylenically unsaturated terminal groups, water-soluble poly(vinyl alcohol), or a mixture of two or more thereof.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 98/22208

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 B41M5/00 C08J7/04 C09D171/02 C09D139/06

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 B41M C08J C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 960 638 A (SHUKU SHIGEKAZU ET AL) 2 October 1990 see column 1, line 38 - column 2, line 2 see column 2, line 23 - column 4, line 66 see column 5, line 3 - line 41 see examples	1-10
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 060 (M-0931), 5 February 1990 & JP 01 286886 A (KANZAKI PAPER MFG CO LTD), 17 November 1989 see abstract	1-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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# INTERNATIONAL SEARCH REPORT

International Application No  
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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 098, no. 002, 30 January 1998 & JP 09 263038 A (MITSUBISHI PAPER MILLS LTD), 7 October 1997 see abstract	1-10
X	PATENT ABSTRACTS OF JAPAN vol. 096, no. 001, 31 January 1996 & JP 07 237347 A (NEW OJI PAPER CO LTD), 12 September 1995 see abstract	1-10

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/22208

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4960638 A	02-10-1990	JP 2001360 A JP 7055581 B	05-01-1990 14-06-1995